

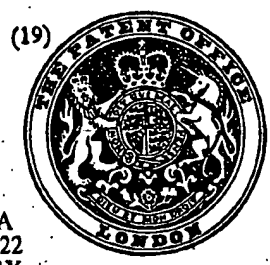
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1 584 428

# PATENT SPECIFICATION

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## (54) HERBICIDES

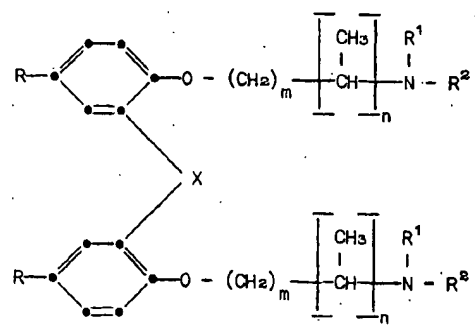
(71) We, ELI LILLY AND COMPANY, a corporation of the State of Indiana, United States of America, having a principal place of business at 307 East McCarty Street, City of Indianapolis, State of Indiana, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention provides novel herbicidal and algicidal compositions and methods making use of a series of aminoalkyl ethers of bis-phenols.

In the prior art, Lacefield *et al.*, *J. Med. Chem.* 14, 133 (1971), teach biphenyloxyalkylamines as useful for inhibiting ADP-induced platelet aggregation *in vitro*. However, there is no teaching to suggest modification of the biphenyl structure to form the compounds of the instant application, nor that the instant compounds would be active as aquatic herbicides or algicides.

Werner, U.S. Patent 3,449,418, teaches the preparation of some of the compounds used in the present invention. Werner, however, discloses the compounds to be useful only as pharmaceuticals and says nothing to suggest that the compounds might be herbicidal or algicidal.

This invention provides a novel method and compositions for reducing the vigor of aquatic weeds or algae which comprises contacting the weeds or algae in water with an herbicidally-effective or algicidally-effective amount of a compound of the formula



wherein

both of R are the same and are hydrogen, halo, nitro, methoxy, or C<sub>1</sub>-C<sub>4</sub> alkyl;

both of R<sup>1</sup> are the same and are hydrogen or C<sub>1</sub>-C<sub>2</sub> alkyl, or -CH<sub>2</sub>CH<sub>2</sub>OH;

both of R<sup>2</sup> are the same and are hydrogen, C<sub>1</sub>-C<sub>4</sub> alkyl, benzyl, cyclohexyl or -CH<sub>2</sub>CH<sub>2</sub>OH;

n is 0 or 1;

when n=0, m=2, 3, or 4;

when n=1, m=2;

X is  $-\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}_2-$ ,  $\text{CH}_3\text{CH}_2-$

or S; or the acid addition salts thereof.

The compositions are in the form of granules wettable powders or an emulsifiable concentrate.

The compounds of Formula I preferred for use in the novel aquatic herbicidal and algicidal compositions and method are those wherein

both of R are the same and are halo or methyl;

both of R' are the same and are hydrogen or  $\text{C}_1-\text{C}_2$  alkyl;

both of R<sup>2</sup> are the same and are  $\text{C}_1-\text{C}_4$  alkyl;

n is 0 or 1;

when n=0, m=2 or 3;

when n=1, m=2;

X is  $-\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}_2-$ , or  $\text{CH}_3\text{CH}_2-$

or the acid addition salts thereof.

The compounds of choice are the following:

2,2' - methylenebis[3 - (p - tolyloxy) - N,N,l - trimethyl - n - propylamine] dihydrochloride

2,2' - methylenebis[3 - (4 - chlorophenoxy) - N,N - dimethyl - n - propylamine] dihydrochloride

2,2' - methylenebis[3 - (4 - chlorophenoxy) - N - (s - butyl) - n - propylamine] dihydrochloride

2,2' - ethylenebis[3 - (4 - chlorophenoxy) - N,N,l - trimethyl - n - propylamine] dihydrochloride

In the above generic formulae,  $\text{C}_1-\text{C}_4$  alkyl refers to straight or branched-chain saturated alkyl i.e. methyl, ethyl, n-propyl, isopropyl, n-butyl, s-butyl, isobutyl, or t-butyl.

Halo is bromo, chloro, or fluoro.

Compounds coming within the scope of the above formulae also include;

2,2' - methylenebis[4 - (4 - bromophenoxy) - N,N - diethyl - n - butylamine] dihydrobromide

2,2' - methylenebis[4 - (4 - fluorophenoxy) - N - methyl - N - (2 - hydroxyethyl) - n - butylamine] dihydrochloride

2,2' - thiobis[2 - (4 - chlorophenoxy) - N - ethyl - N - butyl - ethylamine] dihydrochloride

The novel compounds of Formula I are prepared using starting materials and procedures appearing in the prior art.

The starting materials having a 2,2'-thio linkage are readily prepared by allowing a substituted phenol to react with sulfur dichloride in a suitable solvent, such as carbon tetrachloride. Thus, for example, when 4-chlorophenol is allowed to react with sulfur dichloride, there is obtained 2,2'-thiobis(4-chlorophenol).

The preparation of other starting materials is exemplified by the synthesis of 2,2'-methylenebis(4-methoxyphenol), conveniently prepared by allowing a mixture of 4-methoxyphenol, concentrated aqueous hydrochloric acid, and calcium chloride, in a suitable solvent, such as benzene, to react with paraformaldehyde at from room temperature to 40°C. Other 2,2'-methylenebis(substituted phenol) compounds are prepared by the same general procedure.

Another intermediate, 2,2'-ethylenebis(4-chlorophenol), is synthesized stepwise by following the procedure of Pfleger *et al.*, *Chem. Ber.* 90, 2395-2400 (1957). According to that procedure, 4-chloroanisole is reacted with 37% aqueous formaldehyde solution in the presence of zinc chloride while the mixture is saturated with anhydrous hydrogen chloride at a temperature of 70-80°C., to yield 2-methoxy-5-chlorobenzyl chloride. A portion of that intermediate is reacted with magnesium turnings in ether, and then the remainder of the substituted benzyl chloride is added slowly to the reaction mixture. After the addition is complete, the reaction mixture is refluxed for about 2 hours. The reaction mixture is cooled and aqueous hydrochloric acid (3N) added slowly. The crystalline product which precipitates is 2,2'-ethylenebis(4-chloroanisole). In the third step of the synthesis, the 2,2'-ethylenebis(4-chloroanisole) is allowed to react with a mixture of 48%

aqueous hydrobromic acid and glacial acetic acid to yield the desired 2,2'-ethylenebis(4-chlorophenol).

The 2,2'-thiobis(substituted phenol), 2,2'-methylenebis(substituted phenol), and 2,2'-ethylenebis(substituted phenol) compounds, described *supra*, are utilized in preparing a series of intermediate compounds used in synthesizing the compounds of Formula I.

Thus, for example 2,2'-methylenebis(4-chlorophenol) is allowed to react with 1,3-dibromopropane in the presence of an alkali metal hydroxide in ethanol, and refluxed for four hours. The reaction product mixture is filtered and the filtrate concentrated *in vacuo* to leave a residue, which is then subjected to a vacuum at 100°C., to remove volatile impurities. The residue is the intermediate product, 3,3' - [2,2' - methylenebis(4 - chlorophenoxy)]bis(propyl bromide).

The intermediate 2,2'-methylenebis(substituted phenoxy)bis(alkyl halide) compounds, prepared as described above, are allowed to react with the appropriate amine to prepare the compounds of Formula I.

For example, 4,4' - [2,2' - methylenebis(4 - chlorophenoxy)]bis(butylbromide) is allowed to react with an aminoalkanol, for instance, 2-(ethylamino)ethanol in a suitable solvent, such as ethanol, in a pressure reaction vessel at a temperature of 130—140°C., for a period of time sufficient to bring about substantially complete reaction. The reaction product mixture is worked up by concentrating it *in vacuo* to leave a residue. The residue is made basic with aqueous sodium hydroxide, and the mixture is extracted with a solvent such as chloroform. This solution is in turn extracted with dilute aqueous acid, the aqueous acidic extract made basic, and extracted with a solvent such as chloroform or ether. The extracts are combined, dried, and concentrated *in vacuo* to leave a residue.

This residue is dissolved in a small amount of ethanol, the solution saturated with anhydrous hydrogen chloride, and ether added. The precipitate that separates is recrystallized to yield crystalline 2,2' - methylenebis - [4 - (4 - chlorophenoxy) - N - ethyl - N - (2 - hydroxyethyl) - *n* - butylamine] dihydrochloride. Other of the compounds can be prepared by this same general procedure.

Another process for preparing the compounds of Formula I is illustrated as follows.

The alkali metal salt of a 2,2'-bisphenol or substituted phenol (prepared as previously described), such as 2,2'-methylenebisphenol, is prepared in a suitable solvent, such as ethanol, using an alkali metal alkoxide, such as sodium ethoxide, or an alkali metal hydroxide, such as potassium hydroxide, in methanol, and is isolated by concentrating the solution *in vacuo*. The salt is then suspended in a solvent such as benzene, and to it is added a solution of an aminoalkyl halide, for example, dimethylaminopropyl chloride, and the mixture refluxed overnight. The reaction mixture is worked up by diluting it with water and ether, and separating the organic layer. The nitrogenous base product is isolated via an acid-base work-up in the same manner as described previously, and the product isolated in the form of its acid addition salt, and the product isolated in the form of its acid addition salt. In the present illustration the product isolated is 2,2' - methylenebis - (N,N - dimethyl - 3 - phenoxy - *n* - propylamine) dihydrochloride.

Compounds utilized as starting materials or as intermediates in the preparation of the novel compounds are synthesized by methods known in the art, and described hereinbefore, and these synthesis are exemplified in the following preparations.

#### Preparation 1

##### 2,2'-Thiobis(4-chlorophenol)

A solution of 128 g. of 4-chlorophenol in 250 ml. of carbon tetrachloride was added dropwise to a solution of 51.5 g. of sulfur dichloride in 250 ml. of carbon tetrachloride over a period of 1 hour. The reaction mixture was heated at reflux for 2 hours and then was stirred for 16 hours at ambient room temperature. The material which precipitated was separated by filtration and was recrystallized from benzene, affording 42 g. of yellow leaflets having a melting point of 171—173°C. The product was identified by elemental analyses as 2,2'-thiobis(4-chlorophenol).

Analyses calculated for  $C_{12}H_8Cl_2O_2S$ :

	Theoretical	Found
C	50.18%	50.48%
H	2.81%	2.91%

## Preparation 2

## 2,2'-Methylenebis (4-methoxyphenol)

A mixture of 500 g. of 4-methoxyphenol, 10 ml. of concentrated aqueous hydrochloric acid, 150 g. of calcium chloride and 1.5 l. of benzene was prepared with stirring. To the stirred mixture there was added portionwise, over a period of 5 hours, 60 g. of paraformaldehyde. The rate of addition was adjusted so that the temperature of the reaction mixture did not rise above 40°C. The mixture was stirred for 16 hours at room temperature. The reaction product mixture was filtered and the material on the filter was discarded. The filtrate was washed with water and then dried over anhydrous sodium sulfate. The dried solution was then concentrated *in vacuo* to leave a residue which was distilled at reduced pressure. The forerun was 200 g. of starting phenol. The fraction having a boiling point of 220–235°C./0.05 mm. solidified on standing and was recrystallized three times from benzene-petroleum ether to yield 27 g. of product having a melting point of 78–80°C. The product was identified by NMR spectrum and elemental analyses as 2,2'-methylenebis (4-methoxyphenol).

Analyses calculated for  $C_{15}H_{16}O_4$ :

	Theoretical	Found
C	69.21%	69.16%
H	6.20%	6.14%

## Preparation 3

## 2,2'-Ethylenebis(4-chlorophenol)

This intermediate was prepared according to the procedure of R. Pfeleger *et al.*, *Chem. Ber.* 90, 2395–2400 (1957).

Step 1. A mixture of 270 g. of 4-chloroanisole, 163 g. of 37 percent aqueous formaldehyde solution, and 80 g. of zinc chloride was stirred and warmed to 70°C., and saturated with anhydrous hydrogen chloride gas, while monitoring the temperature and holding the temperature in the range of 70–80°C. After the solution was saturated with the hydrogen chloride gas, the mixture was stirred for an additional 35 minutes and then poured onto a mixture of ice and water. The resulting mixture was extracted with chloroform. The chloroform extracts were combined and dried over anhydrous sodium sulfate. The drying agent was removed by filtration, and the filtrate was distilled to yield 199 g. of colorless product having a boiling point of 128–130°C./10 mm., and a melting point of 47–49°C. The product was identified by elemental analyses and NMR spectrum as 2-methoxy-5-chlorobenzyl chloride.

Analyses calculated for  $C_8H_8Cl_2O$ :

	Theoretical	Found
C	50.29%	50.55%
H	4.21%	4.25%

Step 2. A solution of 199 g. of 2-methoxy-5-chlorobenzyl chloride in 750 ml. of dry ethyl ether was prepared. One hundred ml. of this ethereal solution was added to 14.8 g. of magnesium turnings, and reaction was initiated by the addition of 1 ml. of methyl iodide and warming the mixture. The remainder of the ethereal solution was then added at such a rate that a strong reflux was maintained. When the addition was complete, the reaction mixture was refluxed for 2 hours. At the end of that time, 400 ml. of 3N aqueous hydrochloric acid was added dropwise. After 10% of the acid had been added, most of the material which had precipitated crystallized, causing the ether solvent to boil vigorously. The mixture was filtered and the crystals saved. The filtrate was concentrated *in vacuo* and the crystals from above added to the residue and the whole recrystallized from ethyl acetate to yield 73 g. of product having a melting point of 132–134°C. The product was identified by elemental analyses and NMR spectrum as 2,2'-ethylenebis(4-chloroanisole).

Analyses calculated for  $C_{16}H_{16}Cl_2O_2$ :

	Theoretical	Found
C	61.74%	61.90%
H	5.18%	5.13%

Step 3. A mixture of 10 g. of the product from Step 2, 60 ml. of 48 percent aqueous hydrobromic acid, and 100 ml. of glacial acetic acid was refluxed for 24 hours. The reaction mixture was poured into 1 l. of ice and water and the precipitate was collected by filtration. The precipitate was recrystallized from 100 ml. of benzene to yield 7 g. of product having a melting point of 163–164°C. The

product was identified by elemental analyses and NMR spectrum as 2,2'-ethylenebis(4-chlorophenol).

Analyses calculated for  $C_{14}H_{12}Cl_2O_2$ :

	Theoretical	Found
C	59.36%	58.92%
H	4.24%	4.41%

#### Preparation 4

##### 3,3'-[2,2'-Methylenebis(4-chlorophenoxy)]bis(propylbromide)

A solution was prepared of 135 g. of 2,2'-methylenebis(4-chlorophenol), 66 g. of 85% potassium hydroxide, and 2 l. of ethanol, and to the solution was added 606 g. of 1,3-dibromopropane. The reaction mixture was heated at reflux for 4 hours. The reaction product mixture was filtered and the filtrate concentrated *in vacuo* to leave a residue. The residue was dissolved in ether and washed with 15% aqueous sodium hydroxide and then with water until neutral. The organic layer was then dried over anhydrous sodium sulfate. The drying agent was removed by filtration and the solvent removed *in vacuo* to leave a residue. The residue was subjected to a vacuum of .02 mm. at 100°C., and identified as 3,3'-[2,2'-methylenebis(4-chlorophenoxy)]bis(propylbromide).

The synthesis of the compounds of Formula I are exemplified by the preparations below.

#### Preparation 5

##### 2,2'-Methylenebis(N,N-dimethyl-3-phenoxy-*n*-propylamine) dihydrochloride

To the sodium ethoxide solution prepared by dissolving 0.575 g. of metallic sodium in 50 ml. of commercial absolute ethanol, there was added 10 g. of 2,2'-methylene-bisphenol, and the resulting solution was concentrated *in vacuo* to dryness. The residue thus obtained was suspended in reagent grade benzene, to which suspension, a benzene solution of the free base obtained from 10 g. of dimethylaminopropyl chloride hydrochloride was then added, and the reaction mixture refluxed for 16 hours. The reaction product mixture was worked up by diluting it with water and ether. The ether layer was separated and extracted with dilute aqueous hydrochloric acid. The aqueous acid solution was then cooled, made basic, and extracted several times with ether. The combined ether extracts were dried over anhydrous potassium hydroxide and the drying agent filtered off. The ether filtrate was concentrated *in vacuo* to leave an oily residue. The oily residue was taken up in dry ether and treated with anhydrous hydrogen chloride. The material which precipitated was filtered off and recrystallized from a mixture of ethanol and ethyl acetate to yield product having a melting point of 204–205°C. The product was identified by elemental analyses as 2,2'-methylenebis(N,N-dimethyl-3-phenoxy-*n*-propylamine) dihydrochloride.

Analyses calculated for  $C_{23}H_{34}N_2O_2 \cdot 2HCl$ :

	Theoretical	Found
C	62.29%	62.43%
H	8.18%	8.53%
N	6.32%	5.89%

Following the same general procedure as set forth in Preparation 5, additional compound was prepared and identified. The compound is listed in the Preparation set forth hereinafter.

#### Preparation 6

2,2' - Methylenebis[3 - (4 - chlorophenoxy) - N,N,1 - trimethyl - *n* - propylamine] dihydrochloride

#### Preparation 7

##### 2,2'-Methylenebis[4-(4-chlorophenoxy)*N*-ethyl-*N*-(2-hydroxyethyl)-*n*-butylamine] dihydrochloride

A mixture of 15 g. of 4,4'-[2,2'-methylenebis(4-chlorophenoxy)]bis(butyl bromide) and excess 2-(ethylamino)-ethanol in 100 ml. of commercial absolute ethanol was heated at 140°C., for 10 hours in a pressure reaction vessel. The reaction product mixture was concentrated *in vacuo* to dryness, leaving a residue. The residue was made basic and extracted with chloroform. The chloroform solution was extracted successively with dilute aqueous hydrochloric acid and with

water. The extracts were combined and made basic with aqueous sodium hydroxide, and extracted several times with chloroform. The chloroform extracts were combined and washed with water and dried over anhydrous sodium sulfate. The drying agent was filtered off and the filtrate concentrated *in vacuo*, leaving a residue which was then dissolved in a small amount of commercial absolute ethanol. The ethanol solution was saturated with anhydrous hydrogen chloride and ether was added. The material which precipitated was filtered off and recrystallized from a mixture of ethanol and ether to yield product having a melting point of 154—157°C. The product was identified by elemental analyses as 2,2' - methylenebis[4 - (4 - chlorophenoxy) - N - ethyl - N - (2 - hydroxyethyl) - *n* - butylamine] dihydrochloride.

Analyses calculated for  $C_{28}H_{44}Cl_2N_2O_4 \cdot 2HCl$ :

	Theoretical	Found
C	55.23%	55.28%
H	7.67%	7.26%

Following the same general procedure set forth above, additional compounds were prepared and identified.

20	Preparation 8 2,2' - Methylenebis[3 - (4 - chlorophenoxy) - N - methyl - <i>n</i> - propylamine] dihydrochloride	20
	Preparation 9 2,2' - Methylenebis[3 - (4 - chlorophenoxy) - <i>n</i> - propyl - amine] dihydrochloride	
25	Preparation 10 2,2' - Methylenebis[3 - (4 - chlorophenoxy) - N - cyclohexyl - <i>n</i> - propylamine] dihydrochloride	25
	Preparation 11 2,2' - Methylenebis[3 - (4 - chlorophenoxy) - N - (2 - hydroxyethyl) - <i>n</i> - propylamine] dihydrochloride	
30	Preparation 12 2,2' - Methylenebis[3 - (4 - chlorophenoxy) - N,N - di(2 - hydroxyethyl) - <i>n</i> - propylamine] dihydrochloride	30
35	Preparation 13 2,2' - Methylenebis[3 - (4 - chlorophenoxy) - N - ethyl - N - (2 - hydroxyethyl) - <i>n</i> - propylamine] dihydrochloride	35
	Preparation 14 2,2' - Methylenebis[3 - (4 - chlorophenoxy) - N - ( <i>n</i> - butyl) - <i>n</i> - propylamine] dihydrochloride	
40	Preparation 15 2,2' - Methylenebis[3 - (4 - chlorophenoxy) - N - ( <i>t</i> - butyl) - <i>n</i> - propylamine] dihydrochloride	40
	Preparation 16 2,2' - Methylenebis[3 - (4 - chlorophenoxy) - N,N - di - ethyl - <i>n</i> - propylamine] dihydrochloride	
45	Preparation 17 2,2' - Methylenebis[3 - (4 - chlorophenoxy) - N - isopropyl - <i>n</i> - propylamine] dihydrochloride	45
	Preparation 18 2,2' - Methylenebis[3 - (4 - chlorophenoxy) - N - ( <i>s</i> - butyl) - <i>n</i> - propylamine] dihydrochloride	
50	Preparation 19 2,2' - Methylenebis[3 - (4 - chlorophenoxy) - N - isobutyl - <i>n</i> - propylamine] dihydrochloride	50

	Preparation 20	
	2,2' - Methylenebis[3 - (4 - chlorophenoxy) - N - propyl - n - propylamine]	
	dihydrochloride	
5	Preparation 21	5
	2,2' - Thiobis[3 - (4 - chlorophenoxy) - N - ethyl - n - propyl - amine]	
	dihydrochloride	
	Preparation 22	
	2,2' - Thiobis[3 - (4 - chlorophenoxy) - N - isopropyl - n - propylamine]	
	dihydrochloride	
10	Preparation 23	10
	2,2' - Thiobis[3 - (4 - chlorophenoxy) - N,N - dimethyl - n - propylamine]	
	dihydrochloride	
15	Preparation 24	15
	2,2' - Thiobis[3 - (4 - chlorophenoxy) - N - methyl - n - propylamine]	
	dihydrochloride	
	Preparation 25	
	2,2' - Methylenebis[3 - (4 - chlorophenoxy) - N - benzyl - n - propylamine]	
	dihydrochloride	
20	Preparation 26	20
	2,2' - Methylenebis[3 - (4 - chlorophenoxy) - N - ethyl - n - propylamine]	
	dihydrochloride	
	Preparation 27	
	2,2' - Methylenebis[3 - (4 - methoxyphenoxy) - N,N,1 - trimethyl - n - propylamine]	
	dihydrochloride	
25	Preparation 28	25
	2,2' - Methylenebis[3 - (p - tolyloxy) - N,N,1 - trimethyl - n - propylamine]	
	dihydrochloride	
	Preparation 29	
30	2,2' - Ethylenebis[3 - (4 - chlorophenoxy) - N,N,1 - trimethyl - n - propylamine]	30
	dihydrochloride	
	Preparation 30	
	2,2' - Methylenebis[N,N,1 - trimethyl - 3 - (4 - nitrophenoxy) - n - propylamine]	
	dihydrochloride	
35	Preparation 31	35
	2,2' - Methylenebis[3 - (4 - chlorophenoxy) - N,N - dimethyl - n - propylamine]	
	dihydrochloride	
	Preparation 32	
	2,2' - Methylenebis[2 - (4 - chlorophenoxy) - N,N - dimethylethylamine]	
	dihydrochloride	
40	The compounds have demonstrated activity as aquatic herbicides and algicides, and the novel method of destroying aquatic weeds and algae by the application of these compounds is one embodiment of this invention.	40
45	The novel method of this invention is practiced by adding the chemicals to the water containing the aquatic weeds or algae. The compounds used in this invention kill or inhibit the growth of aquatic weeds and algae when an herbicidally-effective or algicidally-effective amount of one of the compounds is brought into contact with the weeds or algae. Some aquatic weeds float in or on top of water; others are rooted in the underwater soil. Depending on the type of weed of primary concern in a particular body of water, it may be desirable to supply the compound in a form which sinks or floats.	45
50	The method is preferably practiced by adding to the water a sufficient amount of the chemical that a concentration of from 1 to 10 parts per million by weight (0.0001% to 0.001%) is obtained.	50

The optimum concentration for any specific control problem varies with the temperature, the species to be controlled, and the shape of the water body to be treated. At higher water temperatures, less chemical is generally required for a given degree of control than is needed at lower temperatures.

In considering the treatment of moving streams for the purpose of destroying flora therein, special account must be taken of the fact that the chemicals will pass over the area to be treated and that the concentration during the contact period is dependent upon the water flow rate, the rate of chemical addition, and the period of addition.

The compounds are added to the water containing its aquatic weeds or algae in the form of the novel herbicidal and algicidal compositions of this invention. The inert ingredients of the compositions are similar to other agricultural chemical formulations.

Compositions of this invention contain from 0.1% to 90% of the compound, and are in the forms of granules, wettable powders and emulsifiable concentrates. Granules are applied by scattering them over the surface of the water. They may be formulated to sink or float by adjusting the density. In general, granules contain from 0.1 to 10% of the compound, dispersed in or adsorbed on particles of dried earth, stone or sand. Such earths as diatomaceous earth, kaolin, bentonite, montmorillonite, and attapulgite are useful for preparing granules of this invention, and comprise from 90% to 99.9% of the composition.

Wettable powders and emulsifiable concentrates are particularly useful when the composition containing the compound is desired to float, but may be prepared at a high density so that they sink the compound to the bottom of the water. Usually they are applied by dispersing the composition in a relatively small amount of water and spraying the dispersion over the surface of the water. The concentration of the compound in the preliminary dispersion is not important.

Wettable powders comprise an intimate mixture of the active compound in an inert carrier which is a mixture of a fine inert powder and surfactants. The concentration of the active compound is usually from 10 percent to 90 percent by weight. The inert powder is usually chosen from among the attapulgite clays, the montmorillonite clays, the diatomaceous earths, or the purified silicates. Effective surfactants, comprising from 0.5 percent to 10 percent of the wettable powder, are found among the sulfonated lignins, the condensed naphthalenesulfonates, the naphthalenesulfonates, the alkylbenzenesulfonates, the alkyl sulfates, and nonionic surfactants such as ethylene oxide adducts of alkyl phenol.

Typical emulsifiable concentrates of the compounds comprise a convenient concentration of the compound, such as from 50 to 500 g. per liter of liquid, equivalent to from 5 percent to 50 percent, dissolved in an inert carrier which is a mixture of water-immiscible organic solvent and emulsifiers. Useful organic solvents include the aromatics, especially the xylenes, and the petroleum fractions, especially the high-boiling naphthalenic and olefinic portions of petroleum such as heavy aromatic naphtha. Other organic solvents may also be used, such as the terpenic solvents including rosin derivatives, and complex alcohols such as 2-ethoxyethanol. Suitable emulsifiers for emulsifiable concentrates are chosen from the same types and concentrations of surfactants used for wettable powders.

The following formulae illustrate typical exemplary compositions, in which the compounds are identified by their preparation numbers above.

	Granules			
	Example 1			
50	Granulated limestone	95%		50
	Compound 5	4%		
	Cellulose gum	1%		
	Example 2			
55	Granulated kaolin	90%		55
	Compound 28	10%		
	Example 3			
	Silica sand	98%		
	Compound 11	1%		
60	Polybutenes	1%		60



9		1,584,428	9
		Example 4	
	Granulated diatomaceous earth	93%	
	Compound 21	7%	
		Wettable Powders	
5		Example 5	5
	Compound 31	60%	
	Attapulgite	35%	
	Surfactant	5%	
10		Example 6	10
	Compound 13	80%	
	Kaolin	16%	
	Surfactant	4%	
15		Example 7	15
	Compound 16	50%	
	Diatomaceous earth	40%	
	Surfactant	10%	
20		Example 8	20
	Compound 17	90%	
	Purified silicates	6%	
	Surfactant	4%	
		Emulsifiable Concentrates	
25		Example 9	25
	Compound 25	40%	
	Aromatic naphtha	45%	
	Surfactant	5%	
30		Example 10	30
	Compound 20	25%	
	Xylene	70%	
	Surfactant	5%	
35		Example 11	35
	Compound 8	45%	
	Aromatic naphtha	20%	
	2-Methoxyethanol	30%	
	Surfactant	5%	
40		Example 12	40
	Compound 29	15%	
	Xylene	80%	
	Surfactant	5%	
		Solutions	
45		Example 13	45
	Compound 22	30%	
	Water	30%	
	Ethanol	40%	
50		Example 14	50
	Compound 14	12%	
	Water	88%	

The aquatic herbicidal effect of the invention is illustrated by the following trial carried out in the laboratory.

		Trial 1	
50	In this test, the plants used were coontail, <i>Ceratophyllum demersum</i> L.; Florida elodea, <i>Hydrilla verticillata</i> (L.F.); and duckweed, <i>Lemna minor</i> L. The plants were prepared by cutting four-inch terminal sprigs of the coontail and elodea, and		50

selecting approximately enough duckweed to just cover the surface of the water in a 10 ml. beaker (approximately 30 plants). The coontail, elodea and duckweed were then placed in beakers containing 750 ml. of dechlorinated water containing the compounds.

The compounds for this test were formulated in the following manner. Seventeen mg. of compound was weighed into a 12 ml. disposable vial. To the vial containing the compound was added 1 ml. of acetone followed by 10 ml. of aqueous 0.1 percent polyoxyethylene sorbitan monooleate. This stock solution was then pipetted into the beakers at volumes of 0.45 ml. and 4.55 ml., to obtain 1 and 10 ppm. concentration of test compound in 750 ml. of water.

Observations of the effect of the compounds on the plants were made over a seven-day period. The scale for rating the aquatic herbicidal activity of the compounds was on a basis of 1—5, as follows:

- 1=no effect
- 2=slight effect
- 3=moderate effect
- 4=heavy effect
- 5=complete kill

The results of the tests are recorded in Table 1, which follows. Each test compound is identified by its preparation number.

TABLE 1

Compound No.	Appln. Rate ppm.	Hydrilla	Coontail	Duckweed
5	10	5	5	5
	4	1	1	2
	2	1	1	1
	1	4	2	1
9	10	5	5	4
10	1	3	1	1
	10	4	5	5
	4	1	4	5
	2	1	1	4
	1	2	5	3
14	10	5	5	5
	4	1	3	5
	2	1	3	5
	1	4	5	3
15	10	5	5	5
	4	3	4	5
	2	1	2	5
	1	1	5	4
17	10	5	5	5
	4	1	4	5
	2	1	2	5
	1	3	5	4
18	10	5	5	5
	4	3	4	5
	2	2	2	5
	1	5	5	3
19	10	5	5	5
	4	2	2	5
	2	1	1	5
	1	1	4	2
24	10	5	5	5
	1	1	2	1
25	10	4	5	2
	1	3	2	1
28	10	5	5	5
	4	3	2	5
	2	2	1	5
	1	1	2	2

14. A method of Claim 13 wherein the composition comprises a compound wherein

both of R are the same and are halo or methyl;  
 both of R<sup>1</sup> are the same and are hydrogen or C<sub>1</sub>—C<sub>2</sub> alkyl;  
 both of R<sup>2</sup> are the same and are C<sub>1</sub>—C<sub>4</sub> alkyl;  
 n is 0 or 1;  
 when n=0, m=2 or 3;  
 when n=1, m=2;

X is —CH<sub>2</sub>—, —CH<sub>2</sub>CH<sub>2</sub>—, or CH<sub>3</sub>CH<sub>2</sub>—;

or the acid addition salts thereof.

15. A method of Claim 14 wherein the compound is 2,2' - methylenebis[3 - (p - tolyloxy) - N,N,1 - trimethyl - n - propylamine] dihydrochloride.

16. A method of Claim 14 wherein the compound is 2,2' - methylenebis[3 - (4 - chlorophenoxy) - N,N - dimethyl - n - propylamine] dihydrochloride.

17. A method of Claim 14 wherein the compound is 2,2' - methylenebis[3 - (4 - chlorophenoxy) - N - (s - butyl) - n - propylamine] dihydrochloride.

18. A method of Claim 14 wherein the compound is 2,2' - ethylenebis[3 - (4 - chlorophenoxy) - N,N,1 - trimethyl - n - propylamine] dihydrochloride.

19. A method of any of Claims 13—18 wherein the composition supplies to the water from 1 to 10 ppm. of the compound.

20. A composition as claimed in Claim 1 substantially as hereinbefore described with particular reference to any one of the examples.

21. A method as claimed in Claim 13 substantially as hereinbefore described with particular reference to any one of the examples.

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